

# Adsorption of acetanilide herbicides on soils and its correlation with soil properties

Qiquan Wang, Weichun Yang and Weiping Liu\*

Department of Chemistry, Zhejiang University at Yuquan, Hangzhou 310027, PR China

**Abstract:** The adsorption of metolachlor, acetochlor, pretilachlor and butachlor, as a group of acetanilide herbicides, on eight soils with various physical and chemical properties was studied. The adsorption isotherms fit the Freundlich equation well. The extent of adsorption increased in the order: metolachlor < acetochlor < pretilachlor < butachlor. The product of the Freundlich adsorption constants,  $K_f(1/n)$ , showed good correlation with organic matter content (OM) of soils for each of these herbicides, suggesting that the latter is the main factor controlling the adsorption process of these acetanilide herbicides. Multivariate correlation regression between  $K_f(1/n)$  and two factors, water solubility ( $S_w$ ) of herbicides and OM, was also performed.  $K_f(1/n)$  correlated well with  $1/S_w$  and  $OM/S_w$ , showing that high  $S_w$  corresponds to a weak tendency to adsorb on soils. IR spectra and ESR parameters confirmed that multifunctional H bonds and charge-transfer bonds between humic acids (HA) and the herbicides were the main adsorption mechanisms of the latter. The ability of herbicides to form these adsorption bonds with HA increased in the same order as the extent of adsorption.

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**Keywords:** acetanilide herbicide; soil; adsorption; adsorption mechanism; correlation

## 1 INTRODUCTION

Adsorption of herbicides to soil from water is an important factor affecting their fate, biological activity, and persistence in soil. It is affected by various properties of the soil. Better understanding of adsorption and the factors affecting it may make it possible to adjust the herbicide dosage according to soil properties, thus reducing environmental pollution by herbicides.

Acetanilide herbicides are widely used for pre-emergence control of broad-leaved weeds in corn, soybean and several other crops.<sup>1</sup> It has been estimated that the usage of acetanilide herbicides exceeds 100 million pounds per year in the United States.<sup>2</sup> The adsorption of several acetanilides has been studied. The adsorption of metolachlor, acetochlor and alachlor has been found to be closely related to soil organic matter content.<sup>3–5</sup> The adsorption of butachlor was found to increase with soil organic carbon and temperature.<sup>6</sup> Multifunctional hydrogen bonds and charge-transfer bonds were found to be involved in the adsorption of alachlor on humic acids.<sup>7</sup> Little is known about the adsorption of pretilachlor. A direct comparison of adsorption experimental results from different laboratories is difficult because of varying experimental conditions, such as the type of soil, temperature of bath, range of concentration and sampling procedures. Therefore, common rules and

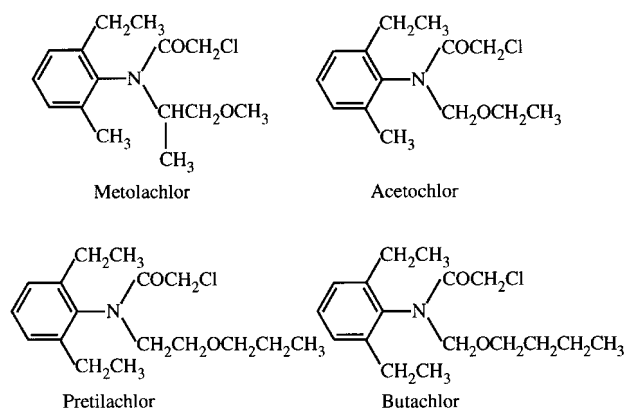


Figure 1. Structures of acetanilide herbicides studied.

quantitative correlation on adsorption of the acetanilide group of herbicides are currently unavailable.

The adsorption of four commonly used acetanilide herbicides, metolachlor, acetochlor, pretilachlor and butachlor, was studied in present work. The structures of these herbicides are shown in Fig 1. Our objectives were (i) to determine and compare the adsorption isotherms of these four herbicides on eight soils with various physical and chemical properties; (ii) to find out by correlation analysis the main factors of soils which affect the adsorption; (iii) to correlate the adsorption with the properties of the herbicides; and

\* Correspondence to: W Liu, Department of Chemistry, Zhejiang University at Yuquan, Hangzhou 310027, PR China

E-mail: wpliu@mail.hz.zj.cn

(Received 12 April 1999; accepted 17 July 1999)

**Table 1.** Selected physical and chemical properties of soils investigated

Soil no	pH	OM	Clay	Silt (%)	Sand	Water	CEC (meq 100g <sup>-1</sup> )
1	7.67	4.0	37.8	48.2	6.1	3.9	30.0
2	4.14	0.64	49.3	31.0	15.6	3.5	15.7
3	6.66	3.4	20.6	43.6	30.4	2.0	12.3
4	7.36	4.3	15.1	44.2	34.4	2.0	17.8
5	4.79	2.8	25.4	40.8	29.3	1.7	6.4
6	4.61	3.8	23.7	34.6	35.8	2.1	10.9
7	5.23	0.25	25.3	32.6	37.1	4.8	34.6
8	8.42	0.71	9.7	83.8	4.4	1.4	8.8

(iv) to determine the adsorption mechanism of these herbicides with the active components of soil.

## 2 MATERIALS AND METHODS

### 2.1 Soil samples and chemicals

Eight soils were used in this study. They were collected in the Zhejiang province of East China. Their physical and chemical properties are summarized in Table 1. The soils were air-dried and sieved to 1 mm. Soil pH was measured in a mixture of soil+water (1+1 by weight) with a glass pH electrode. Particle size distributions were evaluated using the pipette method<sup>8</sup> and the organic matter content (OM) was measured by a colorimetric method using chromic acid.<sup>9</sup> The cation exchange capacity (CEC) was determined by following the procedure reported by Hendershot and Duquette.<sup>10</sup>

Metolachlor (99.2%, purity) was kindly supplied by the Paddy Rice Institute of China. Acetochlor, pretilachlor and butachlor (purity 98, 97.5 and 98.6%, respectively) were supplied by Hangzhou Pesticide Company of China. Methanol was HPLC grade and other chemicals were analytical grade.

Humic acid (HA) was isolated according to conventional procedures<sup>11</sup> from soil no 4.

### 2.2 Herbicide analysis

The concentrations of the herbicides were determined by high performance liquid chromatography (HPLC). A Spectra-Physics Liquid Chromatograph, equipped with a 200×4 mm ID. YWG C<sub>18</sub> (10 µm) analytical column, a Spectra 100 UV-VIS detector and a Super chromatography work station, was used. The flow rate of the mobile phase was 1 ml min<sup>-1</sup>. For detection of metolachlor and acetochlor, the HPLC detector was operating at 230 and 220 nm, and the mobile phase was methanol+water, 70+30 and 75+25 by volume, respectively. Under these conditions, the retention times of metolachlor and acetochlor were 6.50 and 5.00 min, respectively. For pretilachlor and butachlor, the HPLC detector was operated at 227 and 225 nm, and the mobile phase was methanol+water, 85+15 and 82+18 by volume (adjusted to pH 3.0 using phosphoric acid), respectively. Under these conditions, the retention times of pretilachlor and butachlor were 4.86 and 4.83 min, respectively.

### 2.3 Adsorption experiments of soils

Adsorption isotherms were obtained using the slurry-type method. Herbicide solutions (20 ml) were added to 100-ml conical glass bottle with plugs, containing 5.00, 5.00, 2.00 or 0.50 g soil for metolachlor, acetochlor, pretilachlor or butachlor, respectively. The initial concentration of the first three herbicides ranged from 10 to 100 µmol litre<sup>-1</sup>, while that for butachlor ranged from 5 to 50 µmol litre<sup>-1</sup>. The maximum concentrations used were all lower than their water solubility. All experiments were duplicated. Equilibration was achieved by shaking for 24 h at 20(±)2 °C. Preliminary studies showed that, in all cases, adsorption equilibration could be reached within 24 h. The supernatant was then removed by centrifugation at 12000 rev min<sup>-1</sup> for 10 min and stored in stoppered glass vials for HPLC analysis.

### 2.4 Experiments on adsorption mechanisms

Adsorption mechanisms were studied using the interaction products obtained by the method of Senesi.<sup>7</sup> Unreacted HA and its interaction products with each of the herbicides were characterized by infrared (IR) and electron spin resonance (ESR). IR spectra were recorded by a Shimadzu IR-470 using potassium bromide pellets obtained by pressing uniformly prepared mixtures of 1 mg sample and 100 mg potassium bromide under vacuum. ESR spectra were measured on solid samples packed in quartz ESR tubes, using a JES-FEXG ESR spectrometer. Standard samples of Mn and diamond were used as the standard values of spectroscopic splitting factor and free radical concentration (spin/g), respectively.

## 3 RESULTS AND DISCUSSION

### 3.1 Adsorption isotherms of four acetanilide herbicides

Figure 2 shows the adsorption isotherms of these four acetanilide herbicides on eight soils. Their L-shaped isotherms signified that soils had a high affinity for these herbicides, and they were probably adsorbed in a planar position on the surface with multifunctional bonding to soils.<sup>12</sup>

The Freundlich equation is often used for the description of the adsorption of pesticides. The

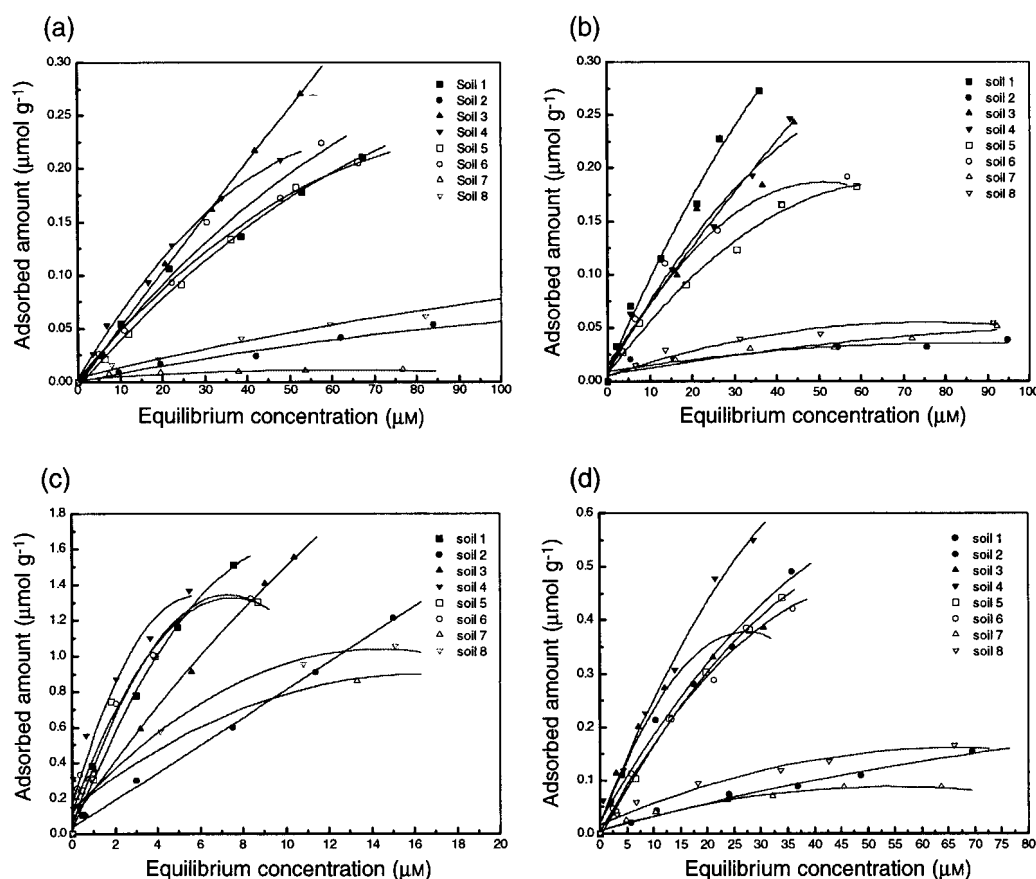


Figure 2. Adsorption isotherms of (a) metolachlor, (b) acetochlor, (c) pretilachlor and (d) butachlor on eight soils.

Table 2. Freundlich constants and correlation coefficients for adsorption of acetanilide herbicides

Soil no	Metolachlor			Acetochlor			Pretilachlor			Butachlor		
	$K_f$	$1/n$	$r$	$K_f$	$1/n$	$r$	$K_f$	$1/n$	$r$	$K_f$	$1/n$	$r$
1	0.00683	0.836	0.982	0.0191	0.734	0.996	0.0384	0.706	0.998	0.281	0.889	0.972
2	0.00158	0.774	0.980	0.0133	0.215	0.954	0.0065	0.740	0.990	0.143	0.751	0.996
3	0.00397	1.070	0.998	0.0135	0.753	0.989	0.0456	0.667	0.972	0.327	0.633	0.995
4	0.01083	0.727	0.997	0.0188	0.658	0.994	0.0367	0.822	0.996	0.690	0.365	0.964
5	0.00393	0.966	0.994	0.0125	0.675	0.995	0.0167	0.952	0.996	0.375	0.587	0.976
6	0.00630	0.877	0.992	0.0154	0.657	0.973	0.0367	0.822	0.997	0.548	0.428	0.999
7	0.00476	0.195	0.981	0.00556	0.465	0.983	0.0106	0.549	0.998	0.355	0.315	0.996
8	0.00395	0.636	0.985	0.00729	0.465	0.960	0.0216	0.491	0.998	0.358	0.409	0.994

Table 3. Correlation coefficients of  $K_f$  ( $1/n$ ) with soil parameters for acetanilide herbicides

Herbicide	pH	$[H^+]$	OM	OM $[H^+]$	Clay	Clay $[H^+]$	CEC	$aOM + bClay$				
Metolachlor	0.385	-0.438	0.942	0.008	-0.311	-0.464	-0.126	$a = 1.30 \times 10^{-3}$ , $b = -3.25 \times 10^{-5}$ , $r = 0.957$				
Acetochlor	0.325	-0.438	0.976	-0.023	-0.087	-0.460	0.009	$a = 2.64 \times 10^{-3}$ , $b = 2.28 \times 10^{-5}$ , $r = 0.978$				
Pretilachlor	0.315	-0.466	0.954	0.059	-0.296	-0.506	-0.148	$a = 6.26 \times 10^{-3}$ , $b = -1.39 \times 10^{-4}$ , $r = 0.966$				
Butachlor	0.299	-0.472	0.974	0.094	-0.252	-0.528	-0.177	$a = 3.43 \times 10^{-2}$ , $b = -5.07 \times 10^{-4}$ , $r = 0.980$				

empirical equation can be expressed as follows:

$$Q = K_f C^{1/n} \quad (1)$$

where  $Q$  is the amount adsorbed by unit mass of soil

( $\mu\text{mol g}^{-1}$ ),  $C$  is the concentration of herbicide in the solution at equilibration ( $\mu\text{mol litre}^{-1}$ ),  $K_f$  and  $1/n$  are constants.  $K_f$  and  $1/n$  are the important parameters in many models for description of environmental fate and transport of pesticides in soils.<sup>13</sup> It was found that the

adsorption isotherms of these four acetanilide herbicides fitted the Freundlich equation well. The values of  $K_f$ ,  $1/n$  and correlation coefficients ( $r$ ) are given in Table 2.

### 3.2 Correlation of adsorption with properties of soil and herbicide

The correlation of adsorption and desorption with soil properties can be used either to predict the adsorption and desorption of pesticides on different soils, or to help determine the factors of soil which dominate in the adsorption and desorption process. The correlation of Freundlich constant  $K_f$  for several pesticides with selected soil parameters has been reported.<sup>4,14–16</sup> The other Freundlich constant,  $1/n$ , is also a very important coefficient for the description of isotherms. The isotherms can differ greatly with change of  $1/n$ . Here,  $K_f(1/n)$  was selected as a parameter of adsorption. Linear regression analysis between  $K_f(1/n)$  and soil parameters was performed. The correlation coefficients ( $r$ ) are listed in Table 3.

For all four herbicides,  $K_f(1/n)$  showed better linear correlation with OM or  $a(\text{OM}) + b(\text{Clay})$  than with other soil parameters. While, overall, correlation with  $a(\text{OM}) + b(\text{Clay})$  was better than that with OM, in most cases the coefficient of OM ( $a$ ) was so much greater than that of Clay ( $b$ ) that the latter term could be omitted. Thus the main property of soil, which dominated in the adsorption process of these acetanilide herbicides, was OM. The linear regression equations of  $K_f(1/n)$  with OM were:

$$K_f(1/n) = 0.000657 + 0.00133 \text{ OM} \quad (2)$$

$$K_f(1/n) = 0.00150 + 0.00261 \text{ OM} \quad (3)$$

$$K_f(1/n) = 0.003425 + 0.00641 \text{ OM} \quad (4)$$

$$K_f(1/n) = 0.1044 + 0.0348 \text{ OM} \quad (5)$$

Equations (2), (3), (4) and (5) correspond to metolachlor, acetochlor, pretilachlor and butachlor, respectively. The gradually increasing intercepts and slopes of these equations indicate that the adsorption extent on soils of these four acetanilide herbicides increased in the order: metolachlor < acetochlor < pretilachlor < butachlor, suggesting that the properties of the herbicide also affect adsorption.

The main difference of these four acetanilide herbicides is in the substituent group of the amide N atom, which is  $-\text{CH}(\text{CH}_3)\text{CH}_2\text{OCH}_3$ ,  $-\text{CH}_2\text{OCH}_2\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$  and  $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  for metolachlor, acetochlor, pretilachlor and butachlor, respectively. Each of these substituent groups contains an ether bond, which is typically regarded as a hydrophilic function. From metolachlor to butachlor, the terminal alkyls of the ether bonds extend gradually, causing the hydrophilic tendency of the ether groups to become weaker and weaker, thus reducing the water-soluble tendency

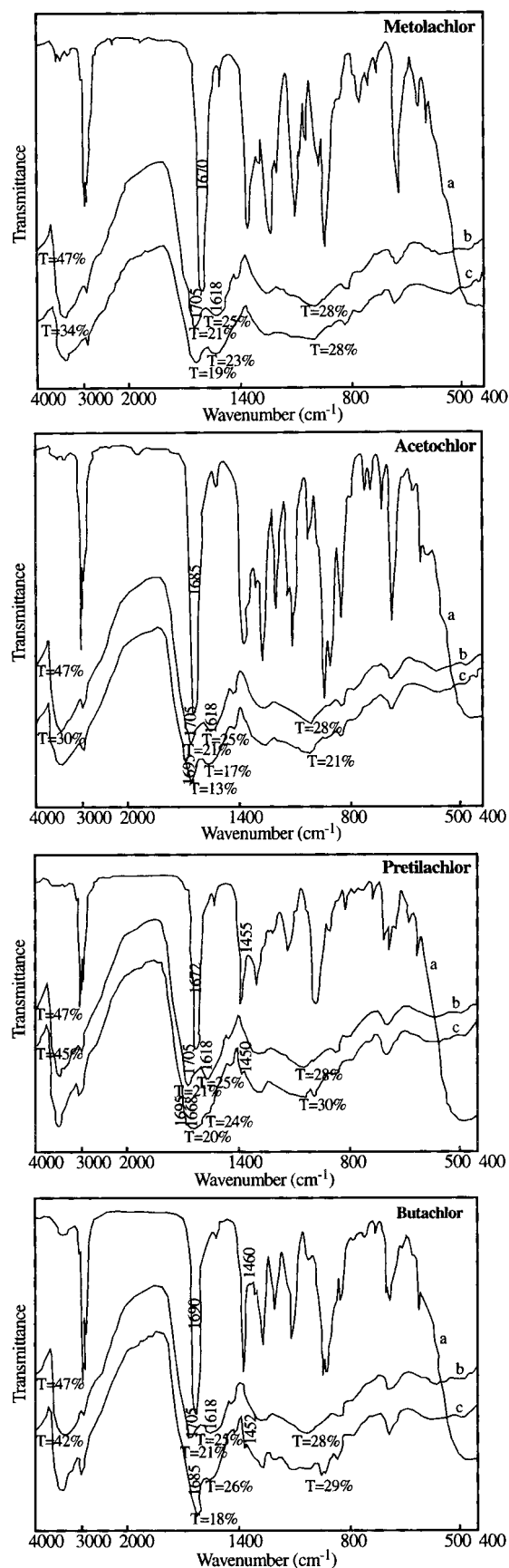


Figure 3. IR spectra of HA and its complexes (a) herbicide (b) HA (c) HA-herbicides complex.

of the whole molecule. This may be an important factor affecting adsorption.

Water solubility ( $S_w$ ) is an important parameter for

Sample	Free radical concentration (spin g <sup>-1</sup> )	Spectroscopic splitting factor (g-value)
HA	$1.608 \times 10^{18}$	2.003
HA-metolachlor	$1.715 \times 10^{18}$	2.003
HA-acetochlor	$1.859 \times 10^{18}$	2.003
HA-pretilachlor	$1.935 \times 10^{18}$	2.003
HA-butachlor	$2.014 \times 10^{18}$	2.003

Table 4. ESR parameters of HA and its complexes

pesticides. It has been found that  $S_w$  has good correlation with  $K_{ow}$  (octanol/water partition coefficient),  $K_{oc}$  and some other parameters.<sup>17</sup>  $S_w$  values for metolachlor, acetochlor, pretilachlor and butachlor are 1868, 826, 160 and 74  $\mu\text{mol litre}^{-1}$ , respectively,<sup>18</sup> in the reverse order to  $K_f(1/n)$ .  $1/S_w$  and  $OM/S_w$  were selected as independent variables for multivariant correlation to incorporate the different intercepts and slopes of the  $K_f(1/n) \sim OM$  regression equations. The regression result showed that  $K_f(1/n)$  had a good correlation with  $1/S_w$  and  $OM/S_w$ . A high correlation coefficient ( $r$ ) of 0.934 was obtained. The regression equation is:

$$K_f(1/n) = -0.0202 + 8.373/S_w + 2.304(OM)/S_w \quad (6)$$

This result indicates that  $K_f(1/n)$  increases with increasing values of  $OM$  and decreasing values of  $1/S_w$ . This suggests that acetanilide herbicides with high  $S_w$  will have a weak tendency to adsorb on soil, while those with low  $S_w$  will have high  $K_f(1/n)$  and adsorb easily to soils.

### 3.3 Adsorption mechanism

Humic acid (HA) is one of the main components of organic matter in soils that performs an important role in adsorption.<sup>19</sup> IR spectra of the pure herbicides, unreacted HA and their interaction products are shown in Fig 3. Because of the small amount of metolachlor and acetochlor adsorbed on HA, there are no pronounced peaks of herbicides in the spectra of the interaction products, but two important changes can be seen by comparing the spectra of pure HA with those of reacted HA. One change is the peak corresponding to the stretching of the C=O group ( $1705 \text{ cm}^{-1}$ ) of HA broadened or shifted to lower wave number ( $1698 \text{ cm}^{-1}$ ), for HA-metolachlor and HA-acetochlor complexes. This may arise from the formation of H bonds between the C=O group of HA and the metolachlor or acetochlor molecules. Another change is the decrease in intensity of the absorption bands in the region of  $1300\text{--}1000 \text{ cm}^{-1}$ , mainly originating from C—O stretching and O—H deformation vibrations of HA. This suggests the involvement of phenolic and alcoholic functions in the H bonding with metolachlor or acetochlor molecules.<sup>20</sup>

Somewhat different peaks from those of HA-metolachlor and HA-acetochlor complexes. appear in

the spectra of HA-pretilachlor and HA-butachlor complexes, providing more information about their adsorption mechanisms. After interaction with pretilachlor, the stretching absorption of the C=O group of both HA ( $1705 \text{ cm}^{-1}$ ) and pretilachlor ( $1672 \text{ cm}^{-1}$ ) shifted toward lower wavenumbers ( $1695 \text{ cm}^{-1}$  and  $1668 \text{ cm}^{-1}$ , for HA and pretilachlor respectively). In the spectra of the HA-butachlor complex, the peaks of the stretching absorption of the C=O group of HA ( $1705 \text{ cm}^{-1}$ ) and butachlor ( $1690 \text{ cm}^{-1}$ ) shifted to  $1685 \text{ cm}^{-1}$ , and overlapped as one peak. This is evidence for the formation of H bonds between the C=O group of HA and the herbicide molecule, and also between the latter and another suitable group in HA. As also seen in the spectra of HA-metolachlor and HA-acetochlor complexes, the decrease of intensity of absorption bands in the region of  $1300\text{--}1000 \text{ cm}^{-1}$  also indicated the occurrence of H bonds between phenolic and alcoholic groups of HA and herbicide molecules.

The peak typically appearing around  $1450 \text{ cm}^{-1}$  is attributed to one of the two peaks caused by stretching of the C=C bond in the aromatic ring. Both of the C=C bond stretching absorption peaks ( $1455 \text{ cm}^{-1}$  for pretilachlor,  $1460 \text{ cm}^{-1}$  for butachlor) appeared in the spectra of HA-herbicide complexes at relatively low wave number ( $1450 \text{ cm}^{-1}$  for HA-pretilachlor,  $1452 \text{ cm}^{-1}$  for HA-butachlor). This result may be ascribed to a decrease in the electron density of the C=C bond of the aromatic ring in the adsorbed herbicide molecule, suggesting the formation of charge-transfer bonds between the electron-donor pretilachlor or butachlor and electron-acceptor components of HA.

ESR is a good approach for the detection of any formation of charge-transfer bonds. Electron transfer, which may take place when an electron donor interacts with an electron acceptor, will generate a charge carrier intermediate of the semiquinone type, stabilizing the resulting charge-transfer system over long periods.<sup>20</sup> Some ESR parameters of unreacted HA and HA-herbicide complexes of this study are listed in Table 4.

Samples of pure herbicides gave no ESR signals. The shapes of ESR spectra of HA-herbicide interaction products, relative  $g$ -factors and line widths did not differ significantly from each other and from those originally observed for unreacted HAs. The same values of  $g$  for all samples indicated that the free radical species in the HA-herbicide complexes was the same

as that in unreacted HA. The enhanced concentration of free radicals in all HA-herbicide complexes relative to that of unreacted HA confirmed the existence of charge-transfer bonds between electron-rich molecules (metolachlor, acetochlor, pretilachlor and butachlor) and electron-deficient HA.

The changes in IR spectra indicated that the downshifted wave number of the peak corresponding to the stretching of the C=O group of HA is 0(broad), 10, 10 and 20 cm<sup>-1</sup>, respectively for HA-metolachlor, HA-acetochlor, HA-pretilachlor and HA-butachlor. This result suggests that the tendency of these herbicides to form H bonds with C=O of HA increased in the order: metolachlor < acetochlor  $\equiv$  pretilachlor < butachlor. Additionally, as shown in Table 4, the free radical concentration increased in the order: metolachlor < acetochlor < pretilachlor < butachlor, suggesting that the ability to form charge-transfer bonds with HA increased in this order.

From these observations, it may be concluded that the ability of herbicides to interact with HA was enhanced in the order: metolachlor < acetochlor < pretilachlor < butachlor, causing the extent of adsorption to increase in the same order.

#### 4 CONCLUSIONS

The L-shaped adsorption isotherms signified that the soil had a high affinity for these four acetanilide herbicides, suggesting that they were probably adsorbed in a planar position on the surface with multi-functional bonding to the soils. The isotherms fitted the Freundlich equation well. The extent of adsorption increased in the order: metolachlor < acetochlor < pretilachlor < butachlor.

Analysis of linear correlation regression showed that the product  $K_f(1/n)$  had a good correlation with organic matter content (OM). OM is the main factor of soil that dominates in the adsorption process.  $K_f(1/n)$  also correlated well with  $1/S_w$  and  $OM/S_w$ , indicating that a high water solubility,  $S_w$ , corresponds to a weak tendency to adsorb on soil for these herbicides. It also suggests that run-off would occur more easily in the soils with low OM for those acetanilide herbicides with high  $S_w$ .

IR spectra and ESR confirmed that H bonds and charge-transfer bonds were the main adsorption mechanisms between these four acetanilide herbicides and HA. It also indicated that the ability of herbicides to interact with HA increased in the order: metolachlor < acetochlor < pretilachlor < butachlor, which caused the extent of adsorption to increase in the same order.

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